EFFECT OF MICROTEXTURE ON COKE VAPOR GASIFICATION
A QUALITATIVE GASIFICATION MODEL

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INTRODUCTION

It is generally accepted that microtexture is one of the keys to the study of many carbonaceous materials (1) and probably one of the most important characteristics of coke in order to provide for its reactivity. So the purpose of this work is to give details on the relation between microtexture and coke reactivity during vapor gasification.

According to Transmission Electron Microscopy studies (1), coke is formed by plane polyaromatic units, also called Basic Structural Units, with local parallel orientation inside a Molecular Orientation domain (M.O. domain). The size of these domains depends on the chemical nature of the precursor (1, 2, 3). As coals are chemically heterogeneous, their cokes contain M.O. domains with varied sizes and their microtexture can be represented by M.O. domains sizes histograms. Ten classes were chosen to form a logarithmic scale: the first three classes corresponding to the smallest M.O. domains (< 15 nm) and classes 9 and 10 corresponding to the largest M.O. domains (> 1 μm).

T.E.M. studies lead to a choice of model of coke microtexture made of "crumpled stacked sheets", where each pore wall is formed by a M.O. domain (1). In the case of carbonaceous materials, it is well known that only the aromatic layer edges (not the layer planes) are reactive (4). Consequently, the smaller the M.O. domain size the larger the free edge density and the more reactive should the material be.

Indeed, previous studies have shown that reactivity was connected to Active Surface Area (i.e. a parameter also connected to the free edge density) (5).

SAMPLING AND MICROTEXTURE CHARACTERIZATION

Six samples were chosen to cover the variety of M.O. domain size (five orders of magnitude from 5 nm to tens of μm) : on one hand, three homogeneous reference cokes without mineral impurities and on the other hand, three heterogeneous cokes from three coals with ashes (Table).

A study by T.E.M. (6) and Small Angle X-ray Scattering (S.A.X.S.) has permitted to caracterize the microtexture. Some results of T.E.M. studies are given in the table (average class and average size of M.O. domains).

S.A.X.S. results presented here are qualitative in nature. Figure 1 presents the scale laws of the three homogeneous cokes and one of the three coal cokes (Vouters). The scale law corresponds to the graph Ln I/Ln $|\vec{s}|$ where I represents experimental scattered intensity and $\vec{s}$ the scattering vector (in reciprocal space) the modulus of which is given by the Bragg's law :

$|\vec{s}| = (2 \sin \theta)/\lambda$ (θ : Scattering angle, λ : wavelength of incident beam).

In the case of Marathon coke, we do not distinguish shoulders or marked peaks in the studied range (1 to 110 nm^{-1}). It appears that we have a similarity of texture at all scales, which was confirmed by previous microscopic observations. Inversely, for the coke of Saran mainly and but also for the coke of Saccharose, we notice the existence of a shoulder around 3 nm. This corresponds to the microporosity described in T.E.M. before. Between these two textural extremes, the coke of Vouters presents an intermediary curve which is not easily interpretable. It is interesting to note the cross checking of microscopic observations with S.A.X.S. data.

APPARATUS

1. Cokefaction

Standardized conditions were specified for the manufacture of the cokes. Samples are pyrolyzed in a Pyrox model oven. The sample (approximatively 5g is placed in a graphite crucible which is itself set inside a Pyrex pipe. The sample is constantly swept by a nitrogen current of 2 l/mn. The heating rate is fixed at 4 K/mn and the final temperature is 1223 K. This temperature was maintained for an hour and then the sample is cooled.

2. Gasification

The powdered coke sample is positioned on a sintered quartz plate held by a quartz tube and placed inside a furnace. The gas flow passes through the sintered plate and the sample. The gases produced by the reaction between the coke and the flowing water mixture are analysed. The main gasification experimental parameters were :

- vector gas pressure : 10^5 Pa
- gasification temperature : 1223 K
- reactive gas : H_2O
- reactive gas concentration : 80%
- vector gas (N_2 + H_2O) flow : 180 l/h (N.T.P.)
- sample weight : 1 g
- grain size : 160-500 µm

So we try to eliminate, as much as possible, parameters extraneous to the effect of microtexture on the gasification processes.

EXPERIMENTAL RESULTS

1. Study of reactivity

Figure 2 presents the evolution of instantaneous reactivity during conversion. By normalizing the integrated reactivity to 100% conversion, a global reactivity scale can be drawn up which follows the scale of increasing M.O. domains size (Figure 3). We can notice that, in our experimental conditions, mineral impurities appear to have no effects on reactivity.

Since the cokes of Vouters and Reden are more reactive than Saccharose coke at the begining of conversion, the evolution of microtexture during gasification was followed in an attempt to understand this difference.

2. Evolution of the microtexture during conversion

Dark-field technique allows one to follow the evolution of M.O. domains size histograms (Figure 4), because the size of M.O. domains does not appear us to change significantly but some M.O. domains preferentially disappear. Thus for heterogeneous cokes, the ratio of the different types of texture change. We have defined three types of texture : small (classes 1 to 3), intermediate (classes 4 to 8) and large (9 and 10) M.O. domains.

Histograms show an increase of the ratio of large M.O. domains. But it appears that intermediate M.O. domains are preferentially burned off, more than small M.O. domains.

DISCUSSION

It can be assumed that global reactivity is the product of "textural intrinsic reactivity" and accessibility to the porosity, which depends on the pore diameter and therefore on the M.O. domain size (if we are in Knudsen regime) (7, 8).

Figure 5 presents the evolution of qualitative gasification model during conversion and Figure 6 illustrates this in the case of a texturally heterogeneous coke (a particle with the three different types of texture).

In the range of large M.O. domains area, accessibility is good but the domains contain only few reactive sites.

In the range of intermediate M.O. domains area, accessibility is still good, reaction takes place inside this texture and a more important number of active sites is present.

When the M.O. domains are small, accessibility is low, reaction occurs only at the circumference of the area, although a very high number of active sites produces strong intrinsic reactivity.

With this qualitative gasification model, we are now able to explain our experimental data : histograms evolution and evolution of instantaneous reactivity during gasification.

In the case of homogeneous cokes of Saran and Saccharose which are constituted only of small M.O. domains, the reactivity increases due to the opening of the pore which increases the accessibility.

In the case of cokes of Vouters and Reden, we have intermediate M.O. domains which give higher reactivity at the begining of conversion. Consequently we have an enrichment in large M.O. domains which stabilizes reactivity.

In the case of coke of Peak-Downs, which is consituted by small and large M.O. domains, reactivity is due only to small M.O.domains, the increase of the ratio large M.O. domains over small M.O. domains also stabilizes reactivity before it decreases. The coke of Marathon, only constituted from large M.O. domains, is not reactive.

CONCLUSION

The samples chosen were representative of practically all the different types of cokes likely to be met. The microtexture of each sample is a key factor in understanding its behaviour during the gasification by water vapor. These first results will be compared to the evolution of microtexture as determined by different independent approaches such as B.E.T. area measurements, and determination of active sites.

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TABLE

Coke of...	Ashes %	Weight %			M.O. domains	
		C	H	O	Average class	Average size (nm)
Saran	0	90,79	2,12	7,09	1	∿ 5
Saccharose	0	95,31	0,55	4,14	2	∿ 10
Vouters	3,6	95,70	0,56	3,73	3,2	∿ 15
Reden	4	96,92	0,44	2,64	6,5	∿ 50
Peak-Downs	15	95,85	2,80	1,36	8,9	∿ 1.000
Marathon	0	99,47	0,17	0,35	10	∿ 100.000

Ash content, weight % (normalized to 100%) and textural parameters of the cokes studied.

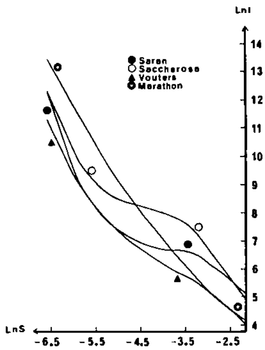

Fig. 1 - Scale laws (S.A.X.S.) of four cokes

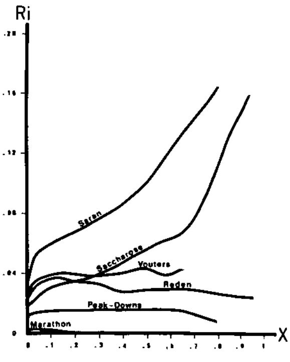

Fig. 2 - Evolution of instantaneous reactivity Ri = 1/m (dX/dt) in $g^{-1}mn^{-1}$ versus conversion (X).

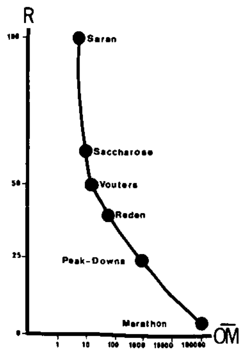

Fig. 3 - Relationship between global reactivity R in arbitrary units versus average size of M.O. domains (O.M.)

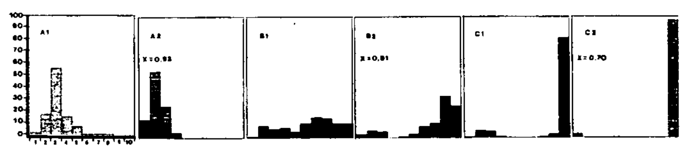

Fig. 4 - Histograms evolution of the M.O. domains size from the heterogeneous cokes of Vouters (a), Reden (b), Peak-Downs (c), before (1) and after (2) gasification, X = conversion.

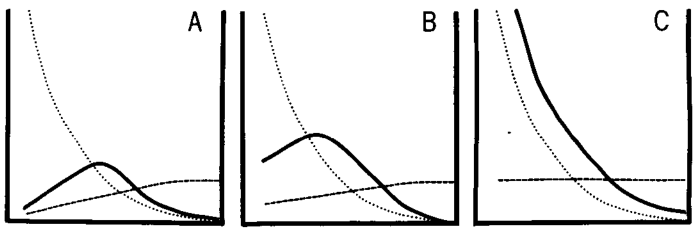

Fig. 5 - Qualitative model for the evolution of the global reactivity (___) during conversion, versus M.O. domains size. Global reactivity is assumed to be the product of the "intrinsic textural reactivity" (...) and the accessibility (---) of porosity.

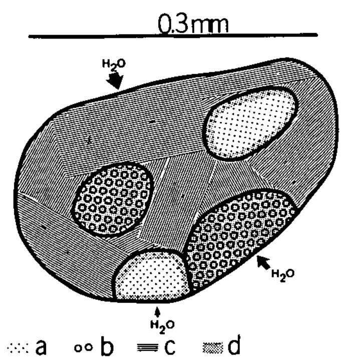

Fig. 6 - Conversion model for coke particles constituted of small (a), intermediate (b) and large (c) M.O. domains, illustrating the difference of accessibility (arrows) and the reactive area (d).